3*d*-shell contribution to the energy loss of protons during grazing scattering from Cu(111) surfaces

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Motivated by a recent experimental work [S. Lederer and H. Winter, Phys. Rev. A **73**, 054901 (2006)] we study the contribution of the 3*d* shell electrons to the energy loss of 100 keV protons scattered off from the Cu(111) surface. To describe this process we use a multiple collision formalism, where the interaction of the projectile with 3*d* electrons is described by means of a sequence of single encounters with atoms belonging to the first atomic layer. In order to compare the theoretical energy loss with the experimental data, we add the contribution of valence electrons, which is evaluated in linear response theory using a response function that incorporates information on the surface band structure. For completeness, the energy lost by protons is also calculated within a jellium model that includes 3*d* and valence electrons with equal footing. Fair agreement between theory and experiment exists when the 3*d* shell is taken into account in the calculation.

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I. INTRODUCTION

In a recent paper [1] measurements of the energy loss for fast hydrogen atoms grazingly colliding with a Cu(111) surface were reported. The experimental data were compared with previous theoretical values [2,3] of the energy lost by protons as a consequence of valence electron excitations and a large discrepancy between theory and experiment was found. The difference was attributed to the contribution of 3*d* electrons of Cu, which constitute an additional channel of electronic excitation not included into the calculations.

In this work we evaluate the energy loss produced by excitation of 3*d* electrons during grazing scattering of protons from a Cu(111) surface. As 3*d* electrons are localized around the surface atoms, to describe this process we employ a theoretical model that represents the electronic transitions induced by the projectile along its trajectory as caused by a succession of single collisions with copper atoms belonging to the first atomic layer [4]. In the model, the ionization probabilities associated with these binary encounters are evaluated within a distorted-wave method—the continuum-distorted-wave-eikonal-initial-state (CDW-EIS) approximation—valid at intermediate and high impact velocities.

Like in the experimental work, we confine our study to 100 keV protons impinging on Cu(111) surfaces with grazing angles. At this impact velocity protons move along the trajectory mainly as bare ions; therefore, the projectile charge state can be considered as fixed [5]. With the aim of comparing our results with the experimental data, we added the contribution of valence electron excitations, calculated within the dielectric formalism. The dielectric function is evaluated in linear response theory using a surface response function that includes detailed information on the band structure of the Cu(111) surface. Atomic units ($e^2=\hbar=m_e=1$) are used unless otherwise stated.

II. THEORETICAL MODEL

When a fast ion grazingly collides with a metal surface, it loses energy as a consequence of the excitation of both conduction electrons of the solid and inner electrons bounded to surface atoms. These mechanisms of energy loss can be evaluated separately. In the case of the Cu(111) surface, as the neutral atom Cu^0 contains only one electron in the outermost shell $n=4$, we consider that the solid atoms cede this electron to the conduction band of the metal, keeping the rest of the electrons in the inner shells. Therefore, we propose that the electron excitation from the 3*d* level is essentially caused by binary collisions between the projectile and topmost atomic cores. Under this assumption and as long as axial surface channeling is not concerned, the energy loss per unit path length traveled by the incident ion, due to electronic transitions from the 3*d* inner shell, is expressed as [6]

$$\frac{dE^{(\mathrm{is})}}{dx} = \delta_s \int_{-\infty}^{+\infty} dy \int d\vec{k}(\varepsilon_{\vec{k}} - \varepsilon_i) P_{\vec{k}}^{(\mathrm{at})}(\rho(\vec{r})), \qquad (1)$$

where $P_{\vec{k}}^{(\mathrm{at})}(\rho)$ is the impact-parameter dependent probability of atomic ionization, which is associated with the ejection of an electron with momentum $\vec{k}$ and energy $\varepsilon_{\vec{k}}=k^2/2$ from the $3d$ initial state, bound to a surface atom with energy ε_i. In Eq. (1), δ_s is the surface atomic density and the impact parameter ρ depends on the position $\vec{r}=(x,y)$ of the considered surface atom, with $\rho(\vec{r})=\sqrt{y^2+Z(x)^2}$, $Z(x)$ the distance of the projectile to the surface, and x (y) the coordinate parallel (perpendicular) to the scattering plane within the surface. For the evaluation of $P_{\vec{k}}^{(\mathrm{at})}$ we employ the CDW-EIS approximation, which is a distorted-wave method that makes use of the CDW and eikonal wave functions, in the final and initial channels, respectively [7]. The CDW-EIS approach takes into account the proper asymptotic conditions, including the distortion produced by the projectile in both the initial and final states. To represent the $3d$ initial state of Cu we used the Hartree-Fock wave function of Ref. [8], while the final continuum state, associated with the electron ejected from the surface atom, was described as a Coulomb wave function with an effective charge satisfying the initial binding energy. Note that at the considered impact energies, transitions from the $3d$ level represent the main mechanism of inner-shell energy loss while contributions coming from deeper shells of Cu atoms can be neglected in the calculation.

The energy loss coming from valence band excitations is evaluated using linear response theory following the model of Ref. [3]. Briefly, the stopping power for a proton traveling parallel at a distance Z from the Cu(111) surface reads as follows:

$$\frac{dE^{(\mathrm{vb})}}{dx}=-\frac{2}{v}\int\frac{d^2\mathbf{Q}}{(2\pi)^2}(\mathbf{Q}\cdot\mathbf{v})\times\mathrm{Im}\{W^{\mathrm{ind}}(Q,Z,Z,\mathbf{Q}\cdot\mathbf{v})\}\Theta(\mathbf{Q}\cdot\mathbf{v}),\qquad(2)$$

where $\mathbf{v}$ is the velocity of the projectile, $v=|\mathbf{v}|$, $\Theta(x)$ is the Heaviside function, and $W^{\mathrm{ind}}(Q,Z,Z,\omega)$ is the Fourier transform of the induced part of the screened interaction, with respect to the two spatial coordinates parallel to the surface and the time. The one-electron wave functions used to calculate the induced response function $W^{\mathrm{ind}}(Q,Z,Z,\omega)$ within the random phase approximation (see [3] for details) are plane waves in the plane parallel to the surface. Along the surface normal, the electronic states are taken as the solutions of the Hamiltonian with an analytic one-dimensional potential, explicitly constructed to reproduce the projected surface band gap of Cu(111) and its surface state [9,10].

Finally, the energy lost by the projectile during the grazing collision is obtained from Eqs. (1) and (2) by integrating $dE^{(j)}/dx$, $j=\mathrm{is},\mathrm{vb}$, along the projectile trajectory. To represent the classical path of the proton we use the surface-projectile potential given by the averaged Ziegler-Biersack-Littmark screening [11,12], which describes the static interaction between the projectile and the crystal surface. Notice that at the present impact energies, the dynamic polarization of the surface might affect the proton trajectory. However, the effect of this interaction was found to be small, except for very grazing incidence angles, lower than 0.5°.

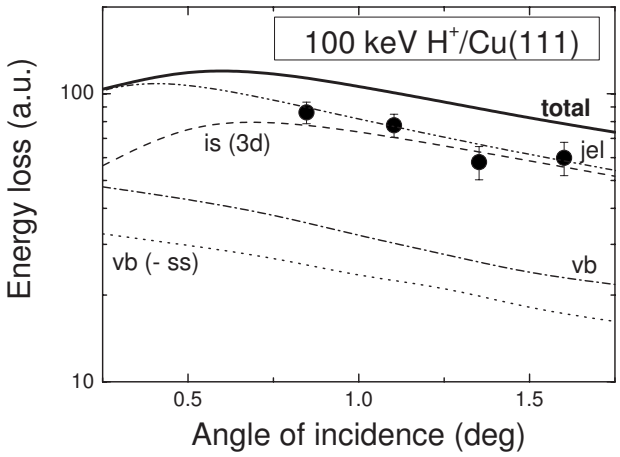

FIG. 1. Energy loss for grazing scattering of 100 keV protons from Cu(111) surfaces, as a function of the incidence angle. Dashed line, inner-shell (is) contribution coming from the $3d$ level; dotted-dashed line, valence-band (vb) contribution; solid line, total energy loss obtained by adding inner-shell and valence-band contributions; dotted-dotted-dashed line, total result derived from the jellium (jel) model; dotted line, valence-band without surface state (vb-ss) contribution. Full dots, experimental data of Ref. [1].

III. RESULTS AND DISCUSSION

In Fig. 1 we display the energy lost by 100 keV protons impinging on a Cu(111) surface, as a function of the incidence angle θ_i, measured with respect to the surface plane. Total results, obtained by adding inner-shell ($3d$) and conduction-band contributions, show an angular dependence similar to the measurements of Ref. [1] but run slightly above the experimental data. As expected, inner-shell ionization from the $3d$ state of Cu is the main mechanism of energy loss, and its importance only decreases when the impact angle diminishes. At large angles of incidence, near the critical angle of penetration in the bulk, the energy loss by valence-band excitations $E^{(\mathrm{vb})}$ is lower by a factor higher than 2 than the inner-shell energy loss $E^{(\mathrm{is})}$. As discussed in Ref. [3], the occupied surface state substantially contributes to $E^{(\mathrm{vb})}$, whose value is strongly reduced when the surface state is not considered in the surface band-structure model. Partial results from the $3d$ shell are in overall accord with measurements. Note, however, that the contribution of $3d$ electrons might be reduced if the screening of the projectile near the surface were included. Besides, our results might be also affected by the fact that Cu atoms were considered as isolated, instead of forming part of a surface.

For the sake of completeness, in Fig. 1 we also display the total energy loss obtained within a jellium model. Since Cu is not a free electron metal, the use of the jellium model is questionable. Nevertheless, it has been shown that the stopping power measurements of ions traveling through different transition metals are well reproduced in the jellium model using an effective number of free electrons N_{eff} [13]. The value of N_{eff} is obtained from experimental data of electron energy loss peaks by means of the free electron gas relation between the plasmon energy and electronic density. In the

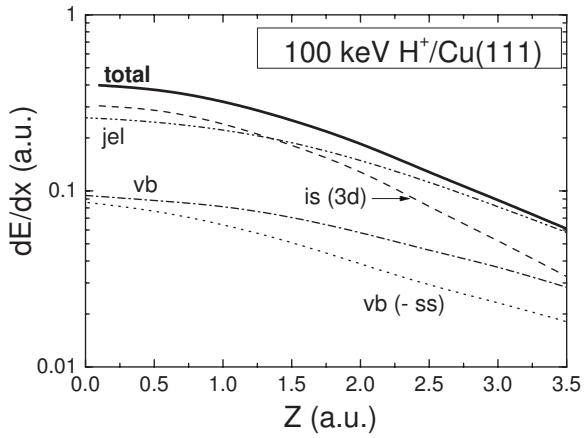

FIG. 2. Energy loss per unit path length, $S=dE/dx$, for scattering of 100 keV protons from Cu(111) surfaces, as a function of the distance Z of the projectile to the topmost atomic layer. Theoretical results, similar to Fig. 1.

case of Cu this value corresponds to $N_{\mathrm{eff}}=3.14$ electrons per atom and $r_s=1.83$ a.u. [14] [where $r_s=(3/4\pi n_0^{\mathrm{eff}})^{1/3}$ and n_0^{eff} is the effective electronic density]. Here, we use this value of r_s to calculate the surface stopping power within the jellium model. Now, the electronic states employed to evaluate the induced response function $W^{\mathrm{ind}}(Q,Z,Z,\omega)$ of Eq. (2) are the Kohn-Sham states obtained in the frame of density functional theory for a jellium surface with $r_s=1.83$ a.u. Remarkably, the energy loss values derived from the jellium model properly reproduce the experimental data, though this model does not include information about the electronic structure of the surface and treats both inner-shell and valence electrons as quasifree electrons bounded at the surface by a finite potential barrier.

To inspect the energy loss mechanisms in more detail, in Fig. 2 we plot the energy loss per unit path length $S=dE/dx$, which is usually called distance-dependent stopping power. Again partial contributions coming from inner-shell and valence excitations are shown in the figure, as a function of the distance Z of the projectile to the topmost atomic layer. The mechanism of ionization from the $3d$ shell prevails in the region close to the crystal surface, where head-on collisions occur, but when the distance to the surface increases, the inner-shell contribution decreases and the excitation of valence electrons becomes important. Note that though the stopping power obtained within the jellium model and the $3d$-electrons contribution display different behaviors for large distances from the surface, both calculations yield very similar energy loss in the angular range corresponding to the experimental data, i.e., $0.75° \lesssim \theta_i \lesssim 1.75°$ (see Fig. 1). This shows that the energy loss in the experiments is governed by the small impact parameter region, where both theories provide similar values.

A stringent test of the theory is given by the energy loss distribution, $dS/d\varepsilon$, as a function of the lost energy ε. Results for $dS/d\varepsilon$ are shown in Fig. 3 for protons moving parallel to the surface, considering two different distances from the topmost atomic layer: $Z=0.5$ and 2 a.u. When the projectile travels close to the surface [Fig. 3(a)], the total energy

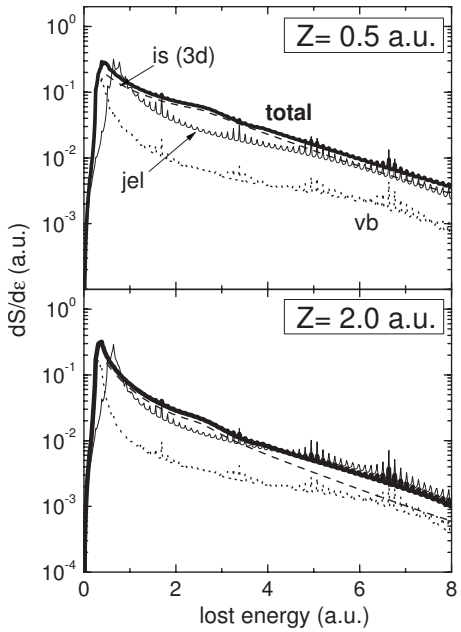

FIG. 3. Energy loss distribution, $dS/d\varepsilon$, as a function of the lost energy ε, for 100 keV protons moving parallel to the Cu(111) surface. Two different distances to the topmost atomic plane are considered: (a) $Z=0.5$ a.u, (b) $Z=2$ a.u. Dashed line, inner-shell (is) contribution coming from the $3d$ level; dotted line, valence-band (vb) contribution; thick solid line, total result obtained by adding inner-shell and valence-band contributions; thin solid line, total result derived from the jellium (jel) model.

loss spectrum—obtained by adding $3d$ shell and valence band contributions—differs from that derived within the jellium model. In particular, in the intermediate energy region, where inner-shell excitations are dominant, the differential total energy loss $dS/d\varepsilon$ decreases slowly, running above the jellium curve. For low transferred energies, instead, the valence spectrum displays a pronounced maximum at $\varepsilon \approx 0.3$ a.u., which corresponds to the surface plasmon frequency. This peak appears shifted towards higher values of ε when the jellium model is employed due to the larger valence electronic density considered within this model. A similar shift of the plasmon peak is also observed in Fig. 3(b). But in this case, for intermediate ε values the discrepancy between both models is smaller. Notice that the oscillatory pattern superimposed to valence and jellium curves is due to the finite width of the box employed for numerical calculations.

IV. CONCLUSIONS

We have presented theoretical results for the energy lost by protons grazingly colliding with a Cu(111) surface, focusing our attention on the inner-shell contribution coming from the $3d$ level. This mechanism was evaluated by assuming that $3d$ electrons remain bound to the topmost atomic cores, and its contribution was found relevant for glancing incidence angles.

To derive the total energy loss we added the contribution due to valence electron excitations, which was obtained

within the linear response theory, including features of the surface band structure. Total results are in agreement with the experimental data, showing a similar behavior as a function of the incidence angle. In addition, we also calculated the energy loss within a jellium model, in which an effective number of free electrons is used to describe the contribution of both 3*d* and 4*s* electrons. Notably, results derived from this simple theory are in good accord with the experiment. Differences between both theoretical approaches are mainly observed in energy loss spectra at energies below 3 a.u.

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